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Hydroboration of Alkenes catalyzed by rhodium compounds

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Hydroboration of Alkenes Catalyzed by Rhodium Compounds

Lu Yang

November 1996

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE

APPROVED BY:

Terrence C. Morrill

Thesis Advisor

Department Head

Library

DEPARTMENT OF CHEMISTRY
ROCHESTER INSTITUTE OF TECHNOLOGY ROCHESTER, NEW YORK

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Title of thesis:**Hydroboration of Alkenes Catalyzed by Rhodium Compounds**

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Date: 11/1996 **Signature of Author:** Lu Yang

ACKNOWLEDGMENTS

I wish to express my sincere thanks to my research adviser Dr. Terence Morrill for his continuous encouragement, guidance and support throughout the research project. My gratitude also goes to my graduate committee, Dr. Marvin Illingsworth, Dr. Kay Turner, and Dr. Laura Tubbs for their help in my graduate research and in the preparation of this thesis. Additionally, I am very grateful for the financial support from the Department of Chemistry at the Rochester Institute of Technology. Finally I would like to thank my family and friends for their continuous support and desire to understand my work.

ABSTRACT

Hydroboration of 1-octene in the presence of $RhCl_3$-Aliquat 336® catalyst for different reaction times (24, 10, 5 and 2 hours), results in 2-octanol as the major product , which means that Markovnikov addition is the major process . Different solvents and temperatures caused some changes of product ratio of 2-octanol to 1-octanol. The same catalyst system has been found to hydroborate styrene in an *anti*-Markovnikov fashion.

1. INTRODUCTION

Hydroboration of alkenes is one of the most widely used reactions in organic synthesis. This reaction was discovered by Herbert C. Brown[1] in the 1950's. Since this discovery, research has been performed in order to understand the reactivity, regioselectivity and the stereoselectivity of hydroborating reagents.

In 1984, Mannig and Noth[2] discovered that using Wilkinson's catalyst[3] [chloro-tris(triphenylphosphine)rhodium] with catecholborane is very effective in enhancing the reactivity and regioselectivity of hydroboration of alkenes. After that, many papers published by other authors, and the main focus of these papers is the comparison of a number of factors such as the regio and stereospecificity of these rhodium catalyzed reactions with uncatalyzed ones. Some of the authors have found that by using Wilkinson's catalyst it is possible to obtain novel results when alkenes are hydroborated.

My research involves studying the uses of complexed $RhCl_3$ as a catalyst to promote the hydroboration of alkenes.

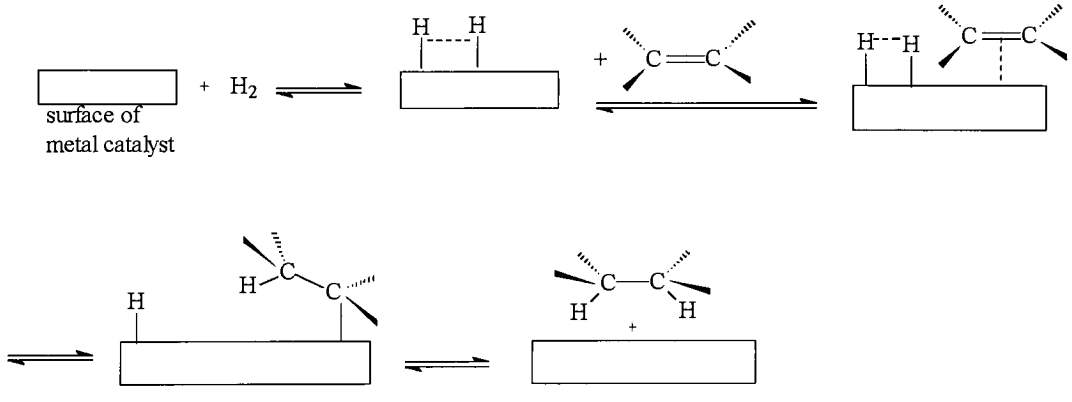
The use of rhodium catalysts for hydroboration is well known. The mechanism of rhodium promotion hydroboration and hydrogenation are very similar to each other, hence it is important to understand the mechanism of rhodium and other metallic catalysts of hydrogenation.

1.1 Heterogeneous and Homogeneous Catalysts

There are two kinds of catalytic processes for hydrogenation of compounds: one is a heterogeneous process the other is a homogeneous process.

In the heterogeneous process the catalyst and the reactants are in different phases, and the catalyst provides a surface where effective interaction of adsorbed reactant molecules can take place. Hence the most effective catalysts are usually those with high surface areas per unit volume (e.g., powders or porous solids). The most commonly used catalysts for hydrogenation are Pt, Ni, Pd, Rh, and Ru.

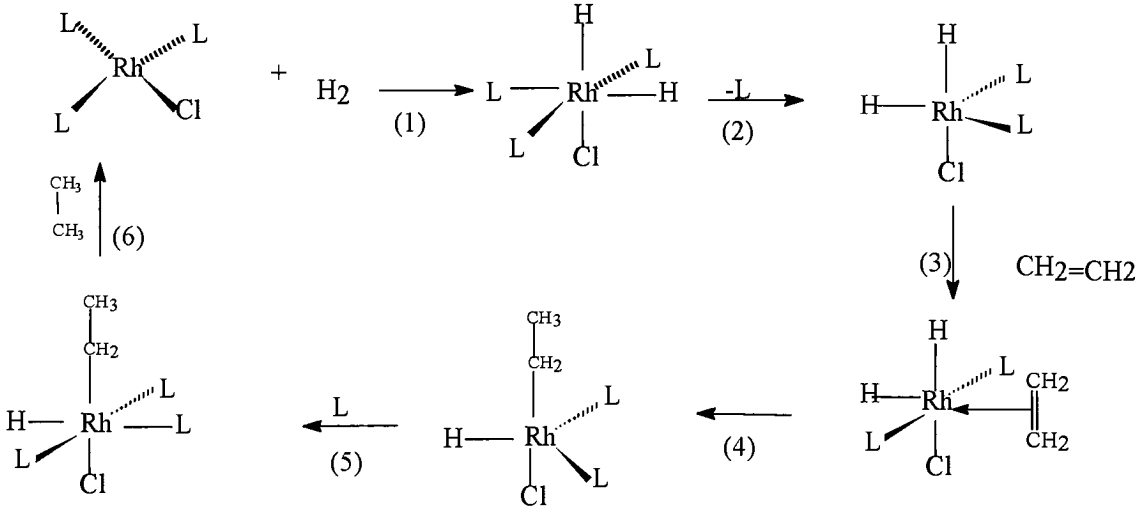
The following is the mechanism of heterogeneous hydrogenation of alkenes[4].



This adsorption of hydrogen can be described in this manner: unpaired electrons on the surface of the metal pair with electrons of hydrogen and bind the hydrogen to the surface. The collision of an alkene with the surface bearing adsorbed hydrogen causes an adsorption of the alkene as well. A stepwise transfer of hydrogen atoms

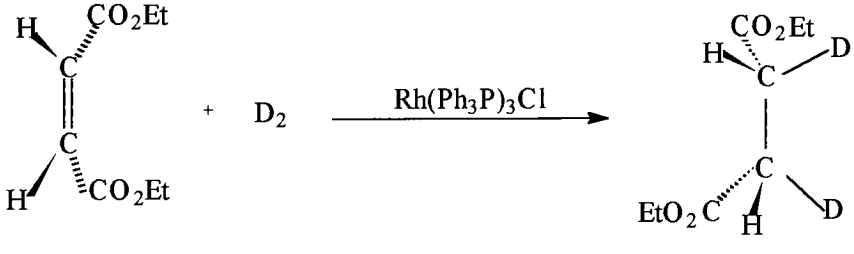
takes place, and this produces an alkane before the organic molecules leaves the catalyst's surface. As a consequence, both hydrogen atoms add from the same side of the double bond, resulting in a *syn* addition.

In the homogeneous catalytic process, the catalyst and the reactant are in the same phase. Most catalytic processes for the heterogeneous hydrogenation of double bonds require the use of high temperature and high pressure. This is not the case for homogeneous processes. The first practical system for the homogeneous reduction of olefins and other unsaturated molecules at 25°C and 1 atmosphere involved the complex $RhCl(PPh_3)_3$ known as Wilkinson's catalyst. The following is the mechanism[5] for the catalytic hydrogenation of olefins.



The first step is oxidative addition: two hydrogens oxidatively add to Wilkinson's catalyst , while the oxidation state of Rh changes from +1 to +3, and the structure of

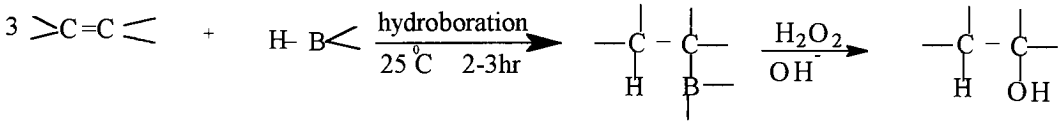
the complex changes from square planar to octahedral. The second step is a ligand dissociation, where one ligand dissociates from the complex, and the structure of the complex changes from octahedral to bipyramidal. The third step is a ligand association, where one alkene molecule associates with the complex and the structure changes from a bipyramid to an octahedron. Step four is an insertion, where the alkene molecule inserts between the rhodium and the hydrogen, the structure of the complex changes from an octahedron to a bipyramid. Step five is ligand association, and here one $P(C_6H_5)_3$ ligand associated with the complex, and the complex then changes from a bipyramid to an octahedron. Step six is a reductive elimination, and an alkane molecule is reductively eliminated from the complex. The oxidation state of the rhodium is changed from +3 to +1, and the structure of the complex changed from octahedral to square planar in step six. Also in step 6 the catalyst is regenerated and this can catalyze hydrogenation of additional alkene by repeating the entire process The insertion in step 4 and the reductive elimination in step 6 are stereospecific (retention), and thus the net result of hydrogenation using Wilkinson's catalyst is a *syn* addition of hydrogen to the alkene. The follow example, where D_2 is in place of H_2 , illustrates this aspect.

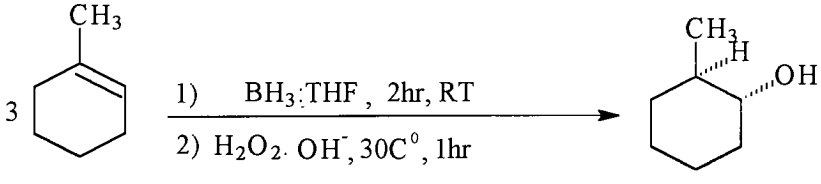


1.2 Normal Hydroborations

Usually the hydroboration of alkenes is carried out using BH_3 in a polar aprotic solvents such as tetrahydrofuran (THF). The role of THF is to convert the dimer form of this reagent, diborane(B_2H_6), to a monomeric form:

Hydroboration can be represented as follows:

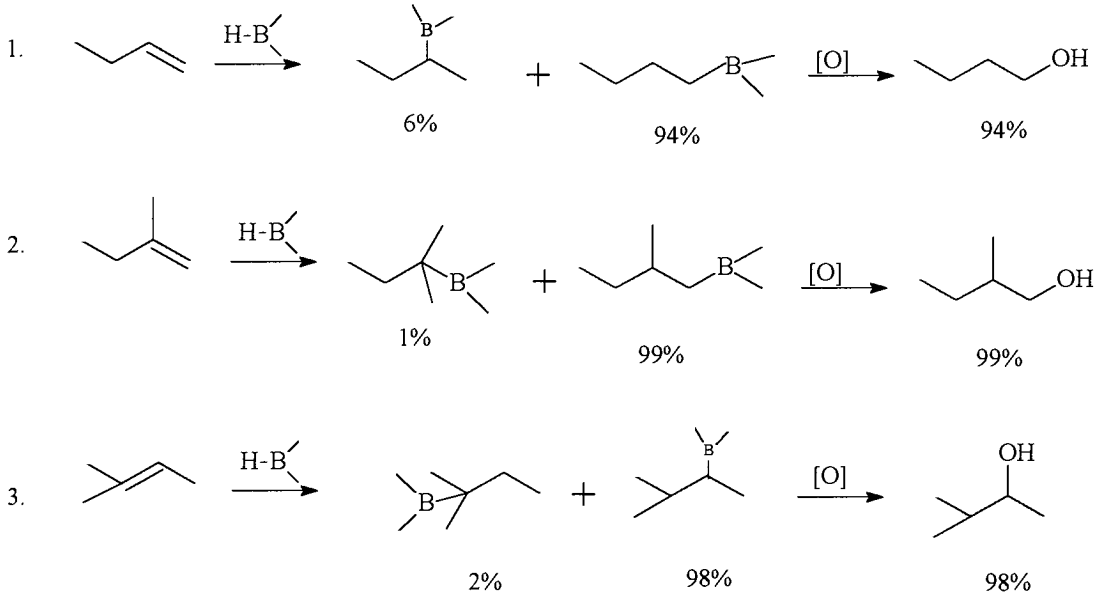




Hydroboration reactions are highly regioselective and stereospecific.

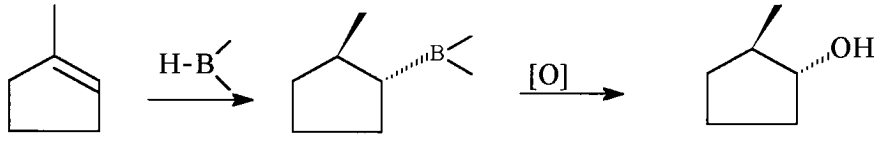
The hydroboration of simple terminal olefins proceeds placement of the boron predominately on the terminal carbon. Consequently, the hydroboration of such ole-

fins, followed by the oxidation provides a means of achieving the *anti*-Markovnikov hydration of alkenes.[6] The following examples illustrate this aspect:



In the first example, 1-butene reacts with the hydroboration reagent, 94% primary oganoborane is formed and only 6% secondary oganoborane is formed. After the oxidation step, 94% primary alcohol is formed. In the second example, 2-methyl 1-butene reacts with the hydroboration reagent, 99% primary oganoborane is formed and only 1% tertiary oganoborane is formed. After the oxidation step, 99% primary alcohol is formed. In the third example, 2-methyl 2-butene reacts with the hydroboration reagent, 98% secondary organoborane is formed and only 2% tertiary oganoborane is formed. After the oxidation step, 98% secondary alcohol is formed.

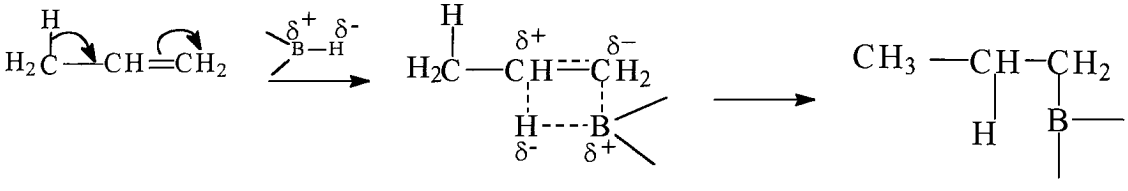
The reaction involves a *syn*-addition of the B-H bond, since the boron atom and the hydrogen atom add to the same face of the double bond.



(pure trans)

The addition takes place preferentially on the less hindered face of the double bond, in an *anti*-Markovnikov fashion.

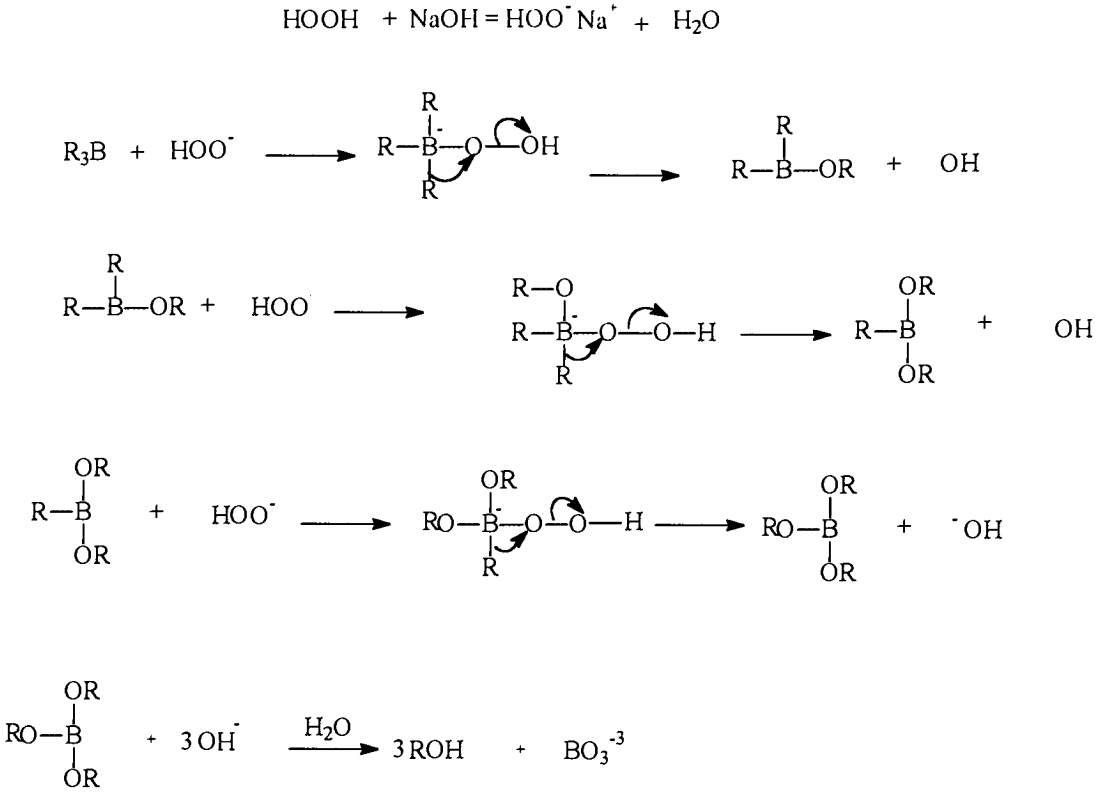
The hydroboration reaction involves a simple four-center transition state[7], with the direction of addition controlled primarily by the polarization of the boron-hydrogen bond.



Borane is an electrophilic species, since it has a vacant 2p orbital and can accept a pair of electrons into that orbital. One source of this electron pair is the π bond of an alkene.

The first step (see above) of the mechanism is the addition of the boron-hydrogen bond to the double bond: this begins with a donation of π electron from the double bond to the vacant p orbital of the boron-hydrogen bond. In the next step, this complex becomes the addition product by passing through a transition state in which the boron atom is partially bonded to the less substituted carbon atom of the double bond and one hydrogen atom is partially bonded to the other carbon atom. As the transition state is approached, electrons shift in the direction of the boron atom and away from the more substituted carbon atom of the double bond. This makes the more substituted carbon atom develop a partial positive charge and since it bears an electron-releasing alkyl group, it is better able to accommodate this positive charge.

The organoboranes produced in the hydroboration step are usually not isolated, instead they are oxidized and hydrolyzed to alcohols by the addition of hydrogen peroxide in an aqueous base. The mechanism is outlined below.[8]

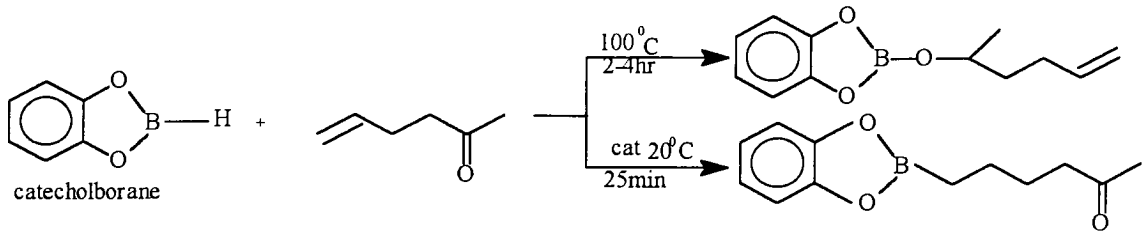


The R-O-B bonds are hydrolyzed in the alkaline aqueous solution, generating the alcohol. The oxidation mechanism involves a series of boron-to-oxygen migrations of the alkyl groups until their electron pairs and thus the stereochemical outcome is conversion of the C-B bond to a C-O bond with *retention of configuration.*

1.3 The Rhodium Catalyzed Hydroboration of Olefins

Hydroboration of alkenes is usually carried out under mild conditions and short periods of time. Catecholborane is an exception, as it is known to be a poor hydroborating reagent, probably due to the unusually electron-rich boron in this compound. It has, however, been found that Wilkinson's catalyst is very effective in enhancing the

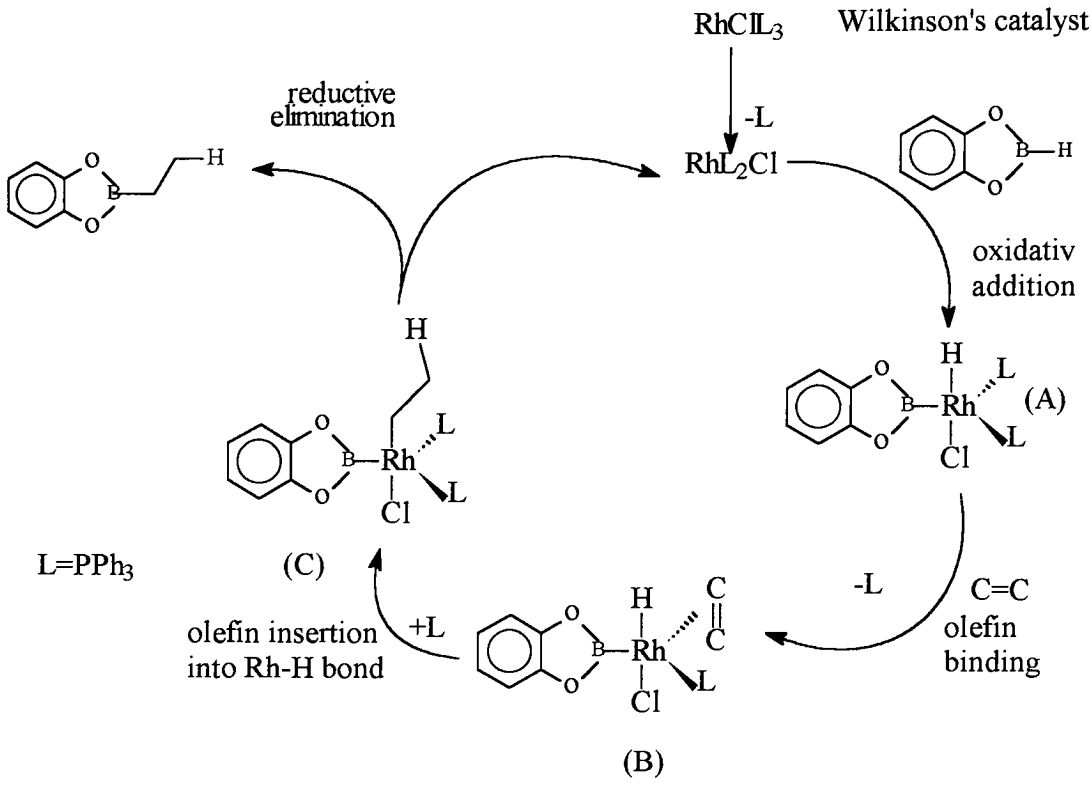
reactivity and regioselectivity of hydroboration of alkenes, using catecholborane. The following two reactions illustrate this behavior[2].



Wilkinson's catalyst: $RhCl[P(C_6H_5)_3]_3$

The first reaction carried out, in the absence of Wilkinson's catalyst at 100 °C for 2-4 hours, caused the carbonyl group of the 3-butenyl methyl ketone to be reduced, while the CC double bond was not reduced. When Wilkinson's catalyst was added to the reaction, it was found that at 20 °C in 25 minutes, the CC double bond of the 3-butene-methyl ketone is preferentially hydroborated and the carbonyl group was not reduced. The two reactions show that Wilkinson's catalyst effectively increased the reactivity of catecholborane, and as well altered the regioselectivity.

Mannig and Noth have proposed this mechanism for olefin hydroboration:[2]

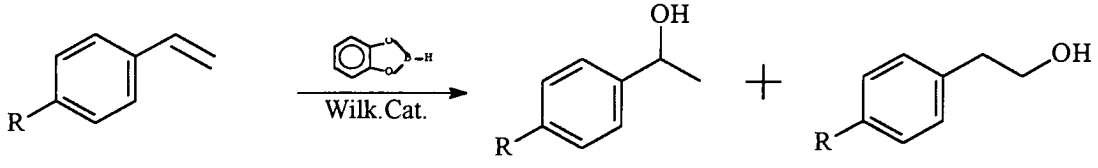


Wilkinson's catalyst is a 16-electron complex, and in solution this complex dissociates one of its triphenyphospine ligands and forms a 14-electron complex. The 14-electron species $RhClL_2$ adds a molecule of catecholborane oxidatively to form a 5-coordinate, 16-electron complex A. One ligand then dissociates from the complex, and this is followed by coordination of an olefin to the complex to form B. The next step of the reaction is an insertion of the alkene into the Rh-H bond as well as the association of one triphenyphospine ligand associates with the complex to form a 5-

coordinate intermediate (C). Then C reductively eliminates to give the organoborane product and reformation of the Wilkinson's catalyst.

The Rhodium Catalyzed Hydroboration of Styrene

In 1990, Lixin Dai[9] and his co-workers found that in the hydroboration of styrene, as well as substituted styrenes, with catecholborane in the presence of Wilkinson's catalyst, the α -alcohol is obtained as the major product. This is an unusual case since Markovnikov, rather than *anti*-Markovnikov hydroboration has occurred.

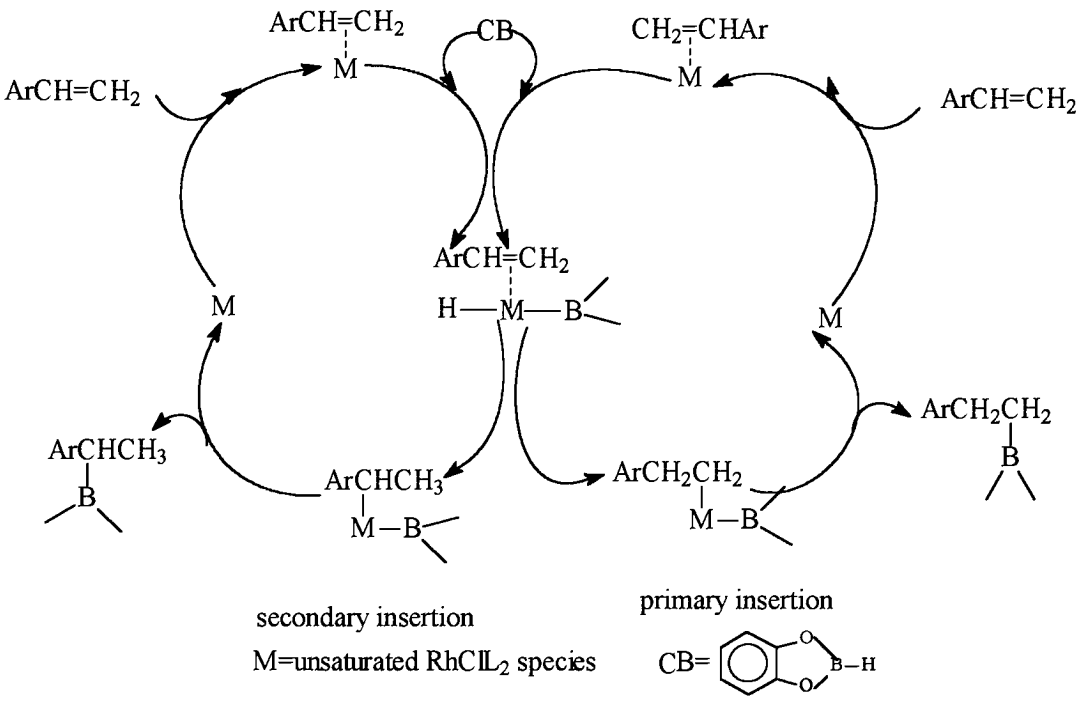


a-c α- alcohol β- alcohol

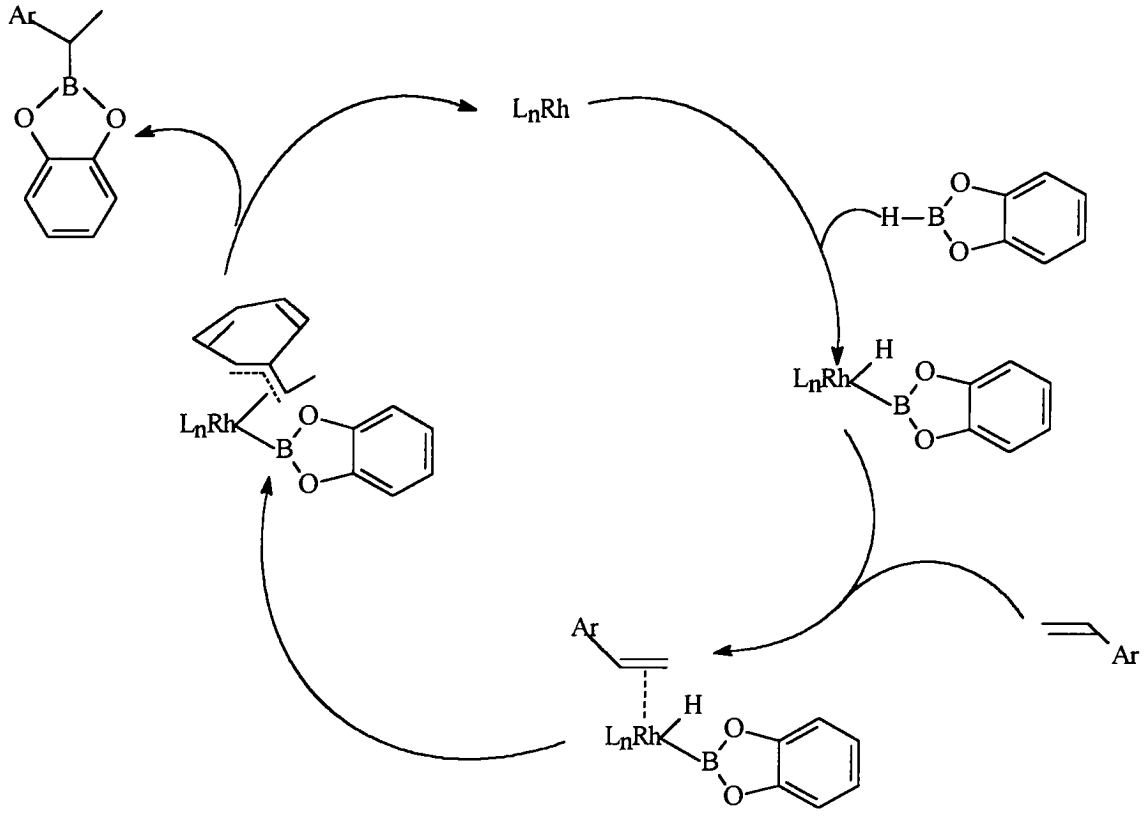
a, R=H; b, R=p-Cl; c, R=p-CH3

There were slightly difference ratios of the α- alcohol to β-alcohol produced by changing the substituent R. The ratios for R equal to H, Cl, and CH_3 , were 86/14, 99/1 and 97/3 respectively.

The catalytic process can be described by the following scheme[9]:



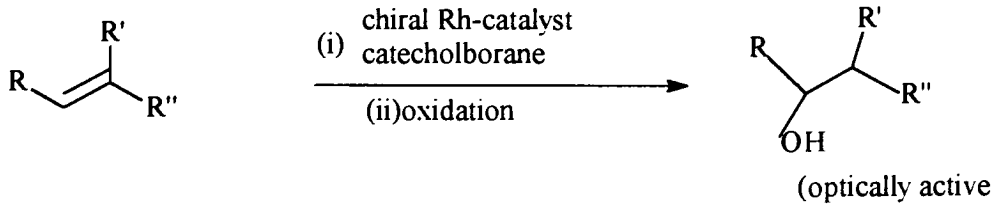
The insertion of an olefin into a M-H bond (or M-B bond) may occur in two different ways: primary insertion or secondary insertion. The secondary insertion displayed here can also be explained by a modified catalytic pathway. This mechanism involves a η^3- benzylrhodium intermediate[10,11]



n = The number of the ligands

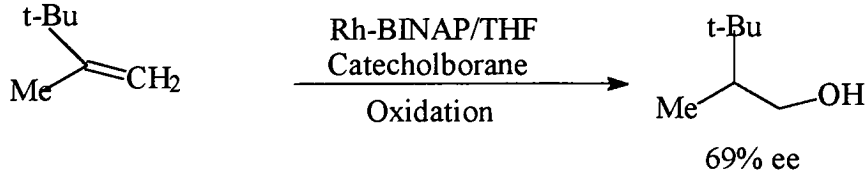
Reductive elimination from the η^3-benzylrhodium intermediate should produce the secondary boronate ester exclusively. Thus the d-orbitals of rhodium interact with the ring π-system, directing the overall addition in a Markovnikov fashion.

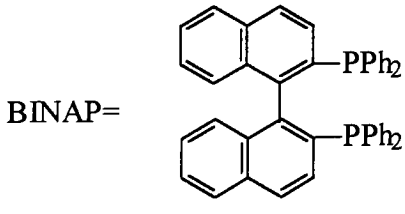
Many applications of rhodium-enhanced hydroborations have been carried out. For example, chiral rhodium-phosphine complexes facilitate enantioselective hydroboration of alkenes by catecholborane; oxidation of the products affords optically active alcohols.[12]



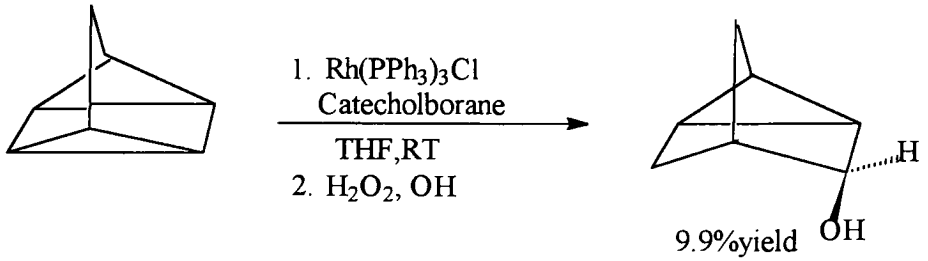
The production of optically active alcohols supports the presence of rhodium-phosphorus complexation necessary for alcohol production.

Burgess and Ohlmeyer[12] found that the use of chiral ligand complexes with rhodium in hydroboration reactions these reactions yield chiral molecules from substrates with varying degrees of enantiomeric excess (% ee). They found that rhodium-catalyzed hydroboration/oxidation of 2,3,3-trimethylprop-1-ene gave the corresponding alcohol in 69% ee.





In 1993 Dr Morrill and his research group found that one hydroboration product of quadricyclene in the presence of Wilkinson's catalyst is nortricyclanol, which is another novel result due to the presence of Rh.[13]

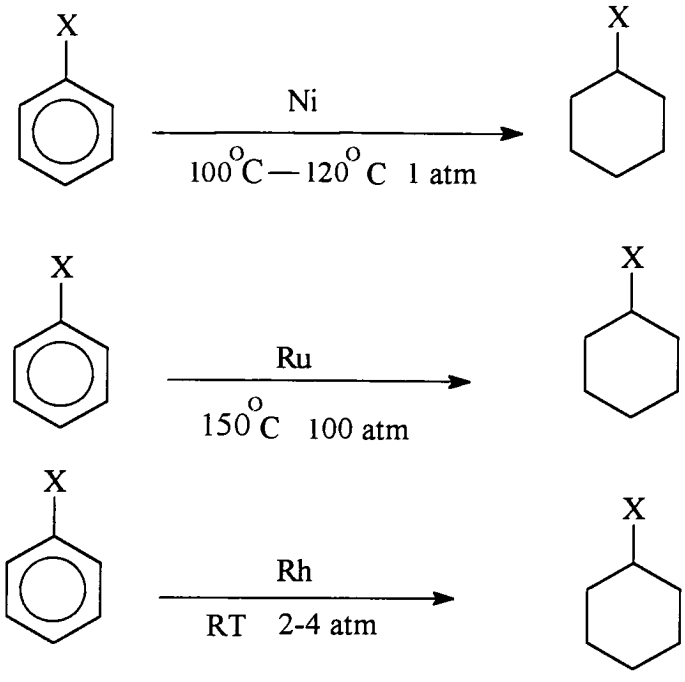


9.9%yield

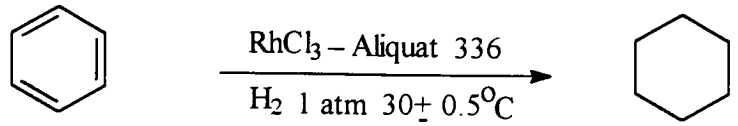
Quadricyclene contains about 96 kcal/mol of strain energy,[14] due to its restricted polycyclic nature. With this amount of ring strain in the molecule, quadricyclene should allow an easy opening of a cyclopropane ring.

1.4 Hydrogenation of Aromatic Compounds in the Presence of $RhCl_3$-Aliquat 336® Ion Pair Catalyst

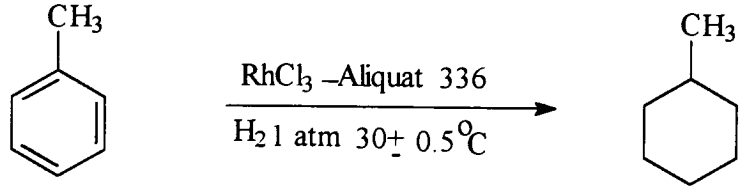
In general aromatic compounds may be reduced to saturated compounds by the process of heterogeneous hydrogenation[15] These reactions are often performed under high temperature and high pressure. Examples are shown below.



In 1983 Blum[16] and his co-workers used the ion pair formed from aqueous rhodium trichloride and Aliquat 336® in dichloroethane to catalyze the hydrogenation of a variety of unsaturated compounds. They found that aromatics were reduced to cyclohexane derivatives under exceedingly mild conditions.

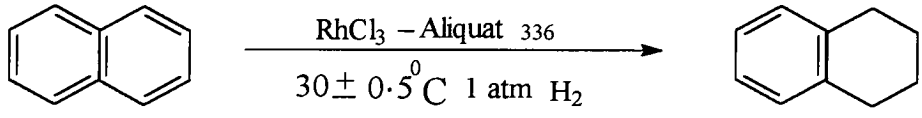


51% yield



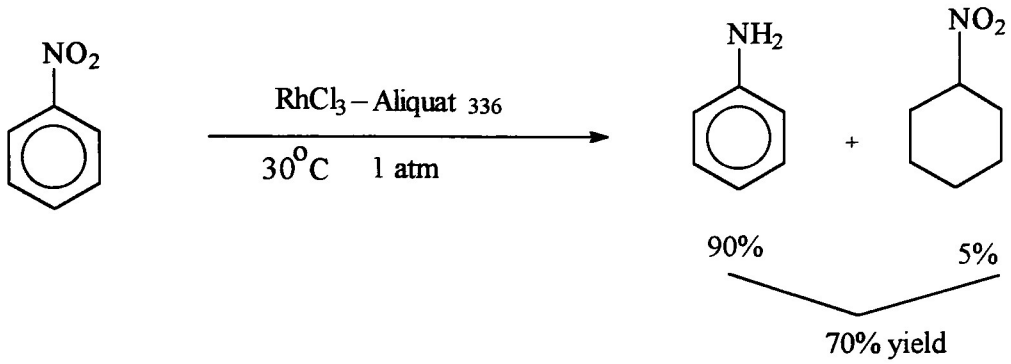
16% yiel

They found that hydrogenation of naphthalene in the presence of the $RhCl_3$ - Aliquat 336® catalyst, produced 1,2,3,4-tetrahydronaphthalene (tetralin) under 30°C and atmospheric hydrogen pressure.[17]



81% yield

In 1987 the same research group reported[18] that the $RhCl_3$-Aliquat336® ion pair catalyzed hydrogenation of nitrobenzene to both aniline and nitrocyclohexane in a two liquid phase system at 30°C.



The yield of the aniline was low, but it is a novel product. The above reaction took place in a phase transfer catalyst promoted process shown below:

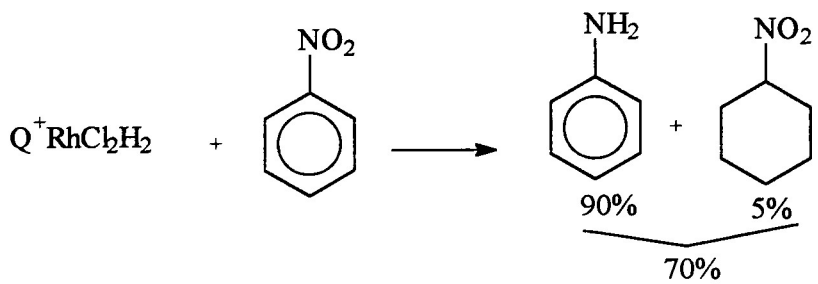
$R_3N^+CH_3\,Cl^-$ + $RhCl_3$ ⇌ $R_3N^+CH_3\,RhCl_4$
(PTC)

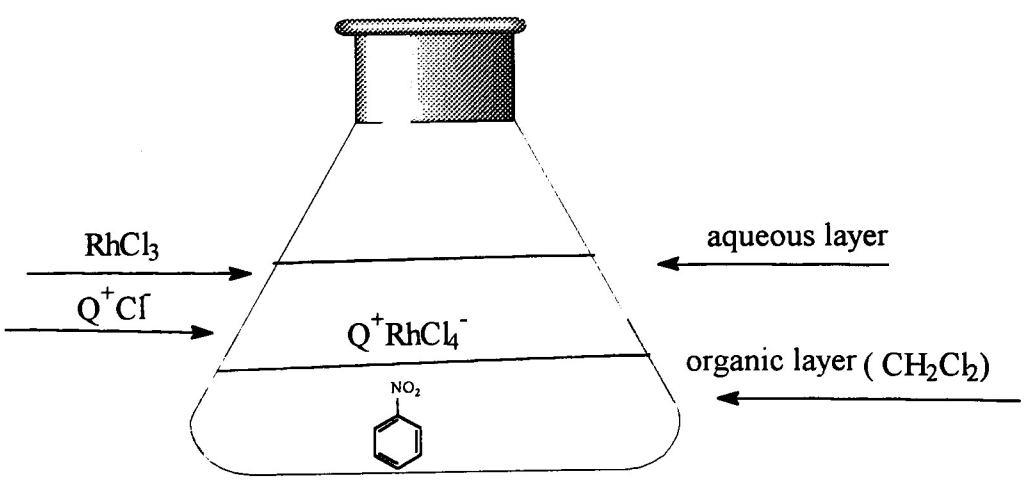
$R_3N^+CH_3\,RhCl_4$ (aq phase) ⇌ $Q^+RhCl_4^-$ (org phase) PTC=Phase Transter Catalyst

$Q^+ = R_3N^+CH_3$

$R=C_8H_{17}$

Q^+RhCl_4 + H_2 ⟶ $Q^+RhCl_2H_2^-$



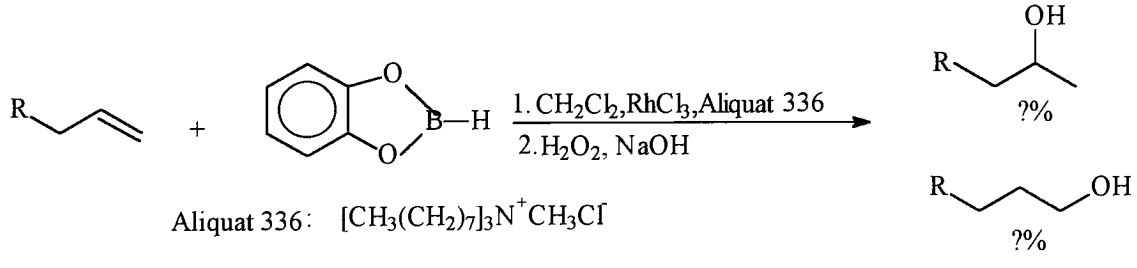


There were two layers in the reaction flask: one was the aqueous layer the other one was the organic layer (CH_2Cl_2). Since methylene chloride is more dense than water, CH_2Cl_2 is the bottom layer. Aliquat 336® combines with $RhCl_3$ to form the ion pair in the water layer. There are three very long alkyl groups in the Aliquat 336® molecule which make the ion pair less polar, and thus the ion pair is transferred from the aqueous layer to the organic layer. Here it combines with H_2 to form the complex which reduces nitrobenzene to produce the aniline / nitrocyclohexane mixture.

2. OBJECTIVE

Hydroboration of unsaturated compounds with Wilkinson's catalyst has produced many novel results. The $RhCl_3$-Aliquat 336® ion pair was used to reduce aromatics to cyclohexane derivatives under extremely mild conditions, and the ion pair was also successfully used for the selective hydrogenation of unsaturated nitroalkenes in a system of two liquid phases at room temperature and atmosphere. Thus it seemed reasonable that the $RhCl_3$-Aliquat 336® system could be used for hydroborations.

The main purpose of my research is to study the ratio of Markovnikov to *anti*-Markovnikov products formed when alkenes or aromatics undergo reaction with catecholborane influenced by the presence of the $RhCl_3$-Aliquat 336® ion pair:



Aliquat 336: $[CH_3(CH_2)_7]_3N^+CH_3Cl^-$

3. EXPERIMENTAL

All chemicals were obtained from the Aldrich Chemical company.

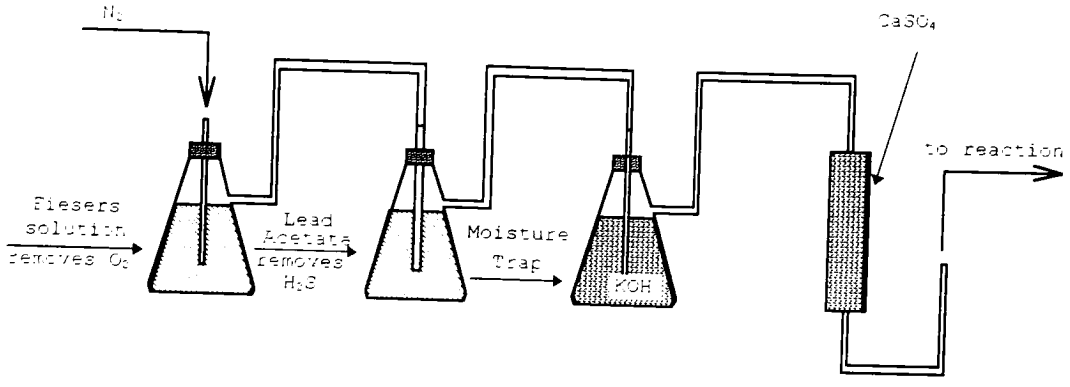
Infrared spectral information was performed on a Perkin Elmer model 1760X Fourier Transform Infrared Spectrometer.

Capillary Gas Chromatography was performed on a Hewlett Packard 5980 series II Gas chromatograph with the following column: HP-5(cross-linked 5% methyl phenyl silicone) 30m x 0.25mm x 0.25 μm film thickness, HP part no, 19091J-433.

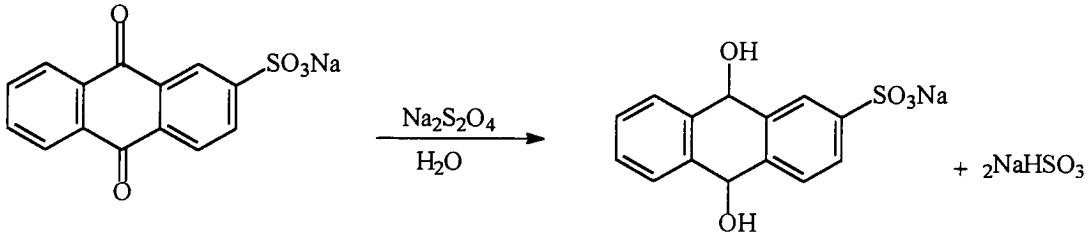
GC-Mass Spectroscopy was performed on a Hewlett Packard model 5995c Gas Chromatography-Mass Spectrometer with the following column: HP-5[poly(5%-diphenyl-95% dimethyl-siloxane)] 30m x 0.25mm x 0.25μm.

^{1}H NMR spectra were obtained from a Bruker 300 MHz in $CDCl_3$.

Fieser's solution[19] was used to absorb traces of oxygen from nitrogen (see figure below).

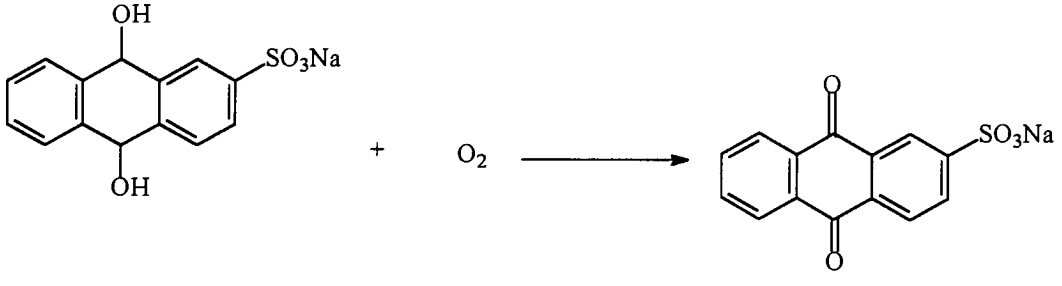


Fieser's solution absorbs oxygen as follows:[20]



sodium anthraquinone- -sulfonate

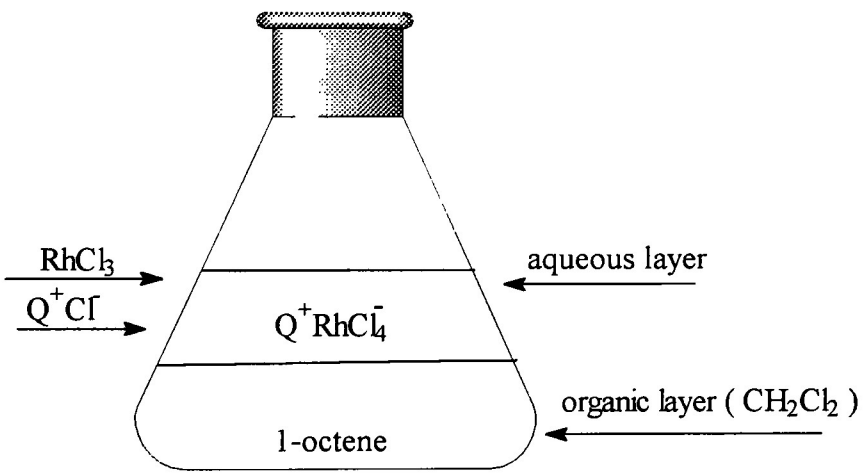
Fieser's Solution



Freshly made Fieser's solution should be clear blood-red in color. A tank of dry nitrogen gas should be used. Traces of oxygen in tank nitrogen are very efficiently re-

moved by the solution. When the color changes to dull red or when a precipitate appears the solution should be replaced.[19] Since the color changes are difficult to detect, the solution should be replaced frequently.

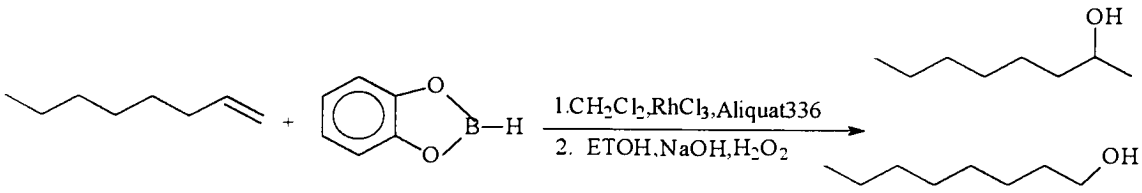
During the initial experiments, a phase transfer catalyst promoted hydroboration of 1-octene was attempted (see figure below):



Q: $(nC_8H_{17})_3N^{+1}CH_3$

Catecholborane decomposed immediately upon coming in contact with water and thus the rest of the reactions were run in organic solvents.

3.1 Procedures for Reaction of 1-Octene with Catecholborane in the Presence of $RhCl_3$-Aliquat 336® Catalyst, Using Methylene Chloride as a Solvent

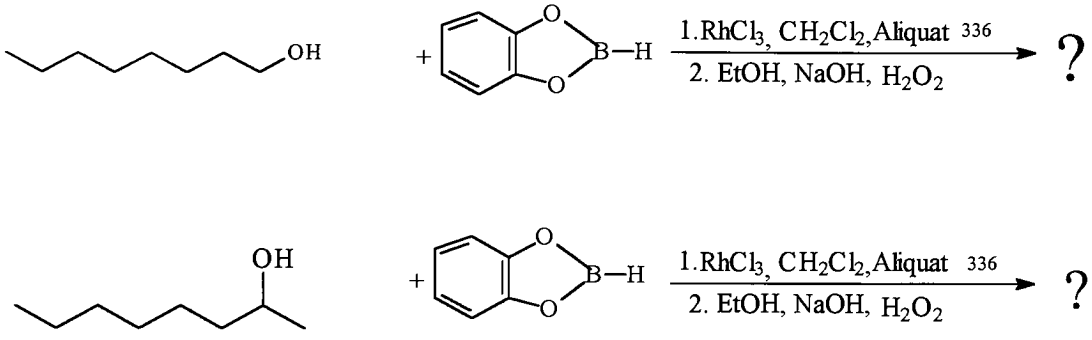


Aliquat 336 : $[CH_3(CH_2)_7]_3N^+CH_3Cl^-$

To a three neck round bottom flask 0.05g of $RhCl_3$, 10 mL of methylene chloride, and 1.6 mL (0.01moles) of 1-octene were added. After about 10 minutes of stirring, some of the $RhCl_3$ was not dissolved and the color of the solution was light pink. At this point, 0.5 mL of Aliquat 336® was added to the solution. After a few minutes, almost all of the $RhCl_3$ was dissolved, and the solution turned raspberry- red in color. The flask was sealed with a septum and purged with dry nitrogen for 5 minutes. The reaction was put in a dry nitrogen box which was previously purged with nitrogen for approximately 10 minutes. Then 0.030 moles (3.2mL) of catecholborane was added dropwise to the flask, and the color of the solution became dark brown. The mixture was stirred for 24, 10 or 5 hours (Table 1 Experiments 7, 8 and 9 on page 36)at room temperature under dry nitrogen. When the reaction was complete, the solution was put in an ice bath and cooled to 5° C, and 15 mL of 95% ethanol was added to quench any excess catecholborane. Then 15 mL of 3M aqueous NaOH followed by 20 mL of 30% hydrogen peroxide were added (H_2O_2 was added dropwise). After stirring for another 24 hours at room temperature, the mixture was filtered first then extracted with three 40 mL portions of diethyl ether and 30 mL of saturated

sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed by using a rotary evaporator. The color of the products was brown suggesting the presence of impurities. The products then were purified by using liquid chromatography. (The stationary phase was silica gel, size 60 A, and the mobile phase was methylene chloride). Fractions were monitored by TLC and the combined alcohol fractions were rotary evaporated to remove most of the methylene chloride. The resulting mixture was pale yellow. This mixture was analyzed by capillary GC, GC-MS, NMR and IR, and the major product was 2-octanol. Experiments 5 and 6 (Table 1) were run with similar conditions as described above, except with an omission of Aliquat 336® Experiment 4 (Table 1) was run with omission of $RhCl_3$. The % yield for experiments 2 and 3 (Table 1) were determined by weighing the concentrated products after rotary evaporation, and the yield for experiments 5-9 (Table 1) were determined by GC using internal standard: 1,3,5-triisopropylbenzene.

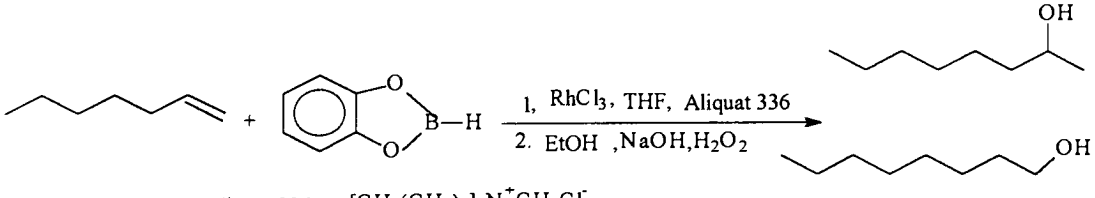
3.2 Kinetic Control: Stability of 1-Octanol and 2-Octanol to Reaction Conditions



The reaction of 1-octene with catecholborane in the presence of the $RhCl_3$-Aliquat 336® catalyst produces 1-octanol and 2-octanol. In order to test the stability of 1-octanol and 2-octanol to reaction conditions and to test whether 1-octanol and 2-octanol interconvert under the reaction conditions, reactions with each of 1-octanol and 2-octanol as starting materials were run under addition conditions as used for the reaction of 1-octene with catecholborane in the presence the $RhCl_3$-Aliquat 336® catalyst. To a dry, 100 mL 3 neck round bottom flask was added 50 mg of $RhCl_3$, 10 mL of methylene chloride, and 1.6 mL (0.01 moles) of 1-octanol or 1.6 mL (0.01 moles of 2-octanol), and this mixture was stirred for a few minutes. Then 0.5 mL of Aliquat 336® was added to the flask, and the solution was stirred until homogeneous. The flask was then purged with dry nitrogen for a few minutes, put in a dry nitrogen box, and 3.2 mL (0.03 moles) of catecholborane were added dropwise to the flask.

The mixture was stirred for 24 hours at room temperature under a dry nitrogen atmosphere. When the reaction was complete, the solution was put in an ice bath and cooled to 5°C, and 15 mL of 95% ethanol was added to quench the excess catecholborane. Then 15 mL of 3M aqueous NaOH followed by 20 mL of 30% hydrogen peroxide were added (H_2O_2 was added dropwise). After stirring for 24 hours at room temperature, the mixture was filtered, extracted with three 40 mL portions of diethyl ether and 30 mL of saturated NaCl (aq) solution. The ether layers were combined and dried over anhydrous magnesium sulfate. The solvent was removed by using a rotary evaporator. The brown color of the products was removed by purification using liquid chromatography (Stationary phase: silica gel; size: 60 A; mobile phase: methylene chloride). This resulted in a pale yellow product mixture this was analyzed by capillary GC. In each case 1-octanol and 2-octanol remained unchanged (Experiments 13 and 14 Table 1).

3.3 Procedures for Reaction 1-Octene with Catecholborane in the Presence of $RhCl_3$-Aliquat 336® Catalyst, Using THF as a Solvent

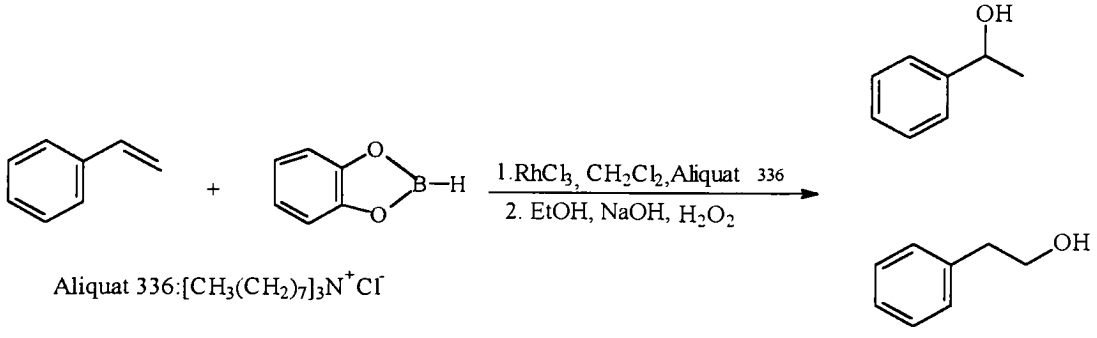


Aliquat 336 : $[CH_3(CH_2)_7]_3N^+CH_3Cl^-$

To a dry 100 mL 3 neck round bottom flask was added 50 mg of $RhCl_3$, 10 mL of THF, and 1.6 mL (0.01 moles) of 1-octene and 2.4 mL (0.01moles) 1,3,5-triisopropylbenzene (the internal standard), and this mixture was stirred for a few minutes, whereupon 0.5 mL of Aliquat 336® was added and the solution was stirred until the solution was homogeneous. The flask was purged with dry nitrogen for a few minutes, put in a dry nitrogen bag, and 0.03 moles of catecholborane were added dropwise to the flask. The mixture was stirred for 10 or 5 hours (Table 2: Experiments 1, 2, and 3, page 41) at room temperature or at 60°C under a dry nitrogen atmosphere. When the reaction was complete, the solution was put in an ice bath and cooled to 5° C, and 15 mL of 95% ethanol was added to quench the excess catecholborane. Then 15 mL of 3M aqueous NaOH followed by 20 mL of 30% hydrogen peroxide were added (H_2O_2 was added dropwise). After stirring for 24 hours at room temperature, the mixture was filtered, extracted with 40 mL of diethyl ether and 30 mL of saturated NaCl solution. The ether layers were combined and dried over anhydrous magnesium sulfate. The solvent was removed by using a rotary evaporator. The brown color of the products was removed by purification using liquid chromatography (The stationary phase: silica gel; size: 60 A; mobile phase : methylene chloride). This resulted in pale yellow products, that were analyzed by capillary GC.

Purification by distillation using a hexadecane chaser was tried, and this was abandoned when the products began to smoke at 60°C under vacuum. The gas chromatogram showed evidence that the alcohols had decomposed by dehydration.

3.4 Procedure for the Hydroboration of Styrene with Catecholborane in the Presence of $RhCl_3$-Aliquat 336® Catalyst, (Methylene Chloride Solvent)



Aliquat 336:$[CH_3(CH_2)_7]_3N^+Cl^-$

To a dry, 100 mL 3 neck round bottom flask was added 50 mg of $RhCl_3$, followed by 10 mL of methylene chloride, and 1.4mL (0.01 moles) of styrene. The mixture was stirred for a few minutes. Then 0.5 mL of Aliquat 336® was added to the flask and the solution was stirred until the $RhCl_3$ dissolved. The solution was purged with dry nitrogen for a few minutes and put in a dry nitrogen box and 0.03 moles of catecholborane was added by syringe. The mixture was stirred for 5 hours at room temperature under dry nitrogen atmosphere. When the reaction was complete, the solution was put in an ice bath and cooled to 5° C, and 15 mL of 95% ethanol was added to quench the excess catecholborane. Then 15 mL of 3M aqueous NaOH followed by 20 mL of 30% H_2O_2 were added (H_2O_2 was added dropwise). After stirring the mixture for 24 hours at room temperature, it was filtered first then extracted with three 40 mL portions of diethyl ether and 30 mL of saturated NaCl solution. The ether layers were combined, dried over anhydrous magnesium sulfate, and the solvent

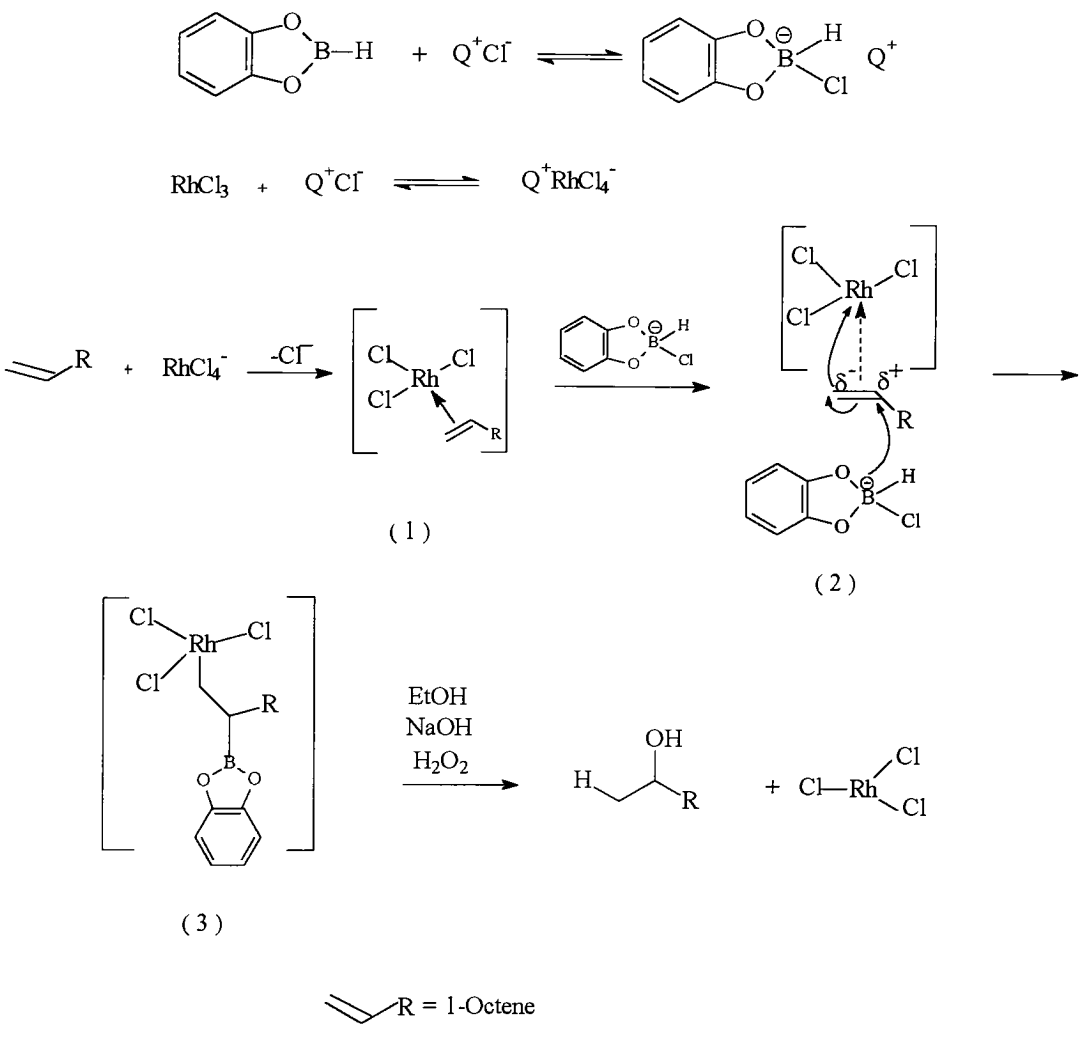
was removed by using a rotary evaporator. Some of the brown color of the products was removed using liquid chromatography purification (Stationary phase: silica gel; size: 60 A; mobile phase : methylene chloride). Fractions were monitored by TLC and the combined alcohol fractions were rotary evaporated to removed most of the methylene chloride. After this the color of the products was pale yellow. The products were analyzed by capillary GC, IR and NMR.

4. RESULTS AND DISCUSSION

The hydroboration of 1-octene with catecholborane in the presence of Wilkinson's reagent, under room temperature run for 8 hours, gave 1-octanol (97.8%) as the major product and 2-octanol (2.22%)[21] as the minor product (with an overall yield 78.5 %). This ratio is essentially the same as found for the hydroboration reaction with BH_3:THF in the absence of rhodium catalyst that is the reaction proceeded *anti*-Markovnikov fashion.

When 1-octene underwent reaction with catecholborane in the presence of $RhCl_3$ and Aliquat 336® ion pair, the major product was often 2-octanol (Table 1: Experiments 1, 2, 3, 7, 8, 9, 10, 11 and 12 on page 36) which indicated that Markovnikov addition had occurred. Thus a combination of $RhCl_3$ and Aliquat 336® catalyst has led to a novel hydroboration reaction as we have achieved Markovnikov hydroboration of an alkene that bears no aryl groups.

The proposed mechanism is the following:



In solution, a chloride ion from Aliquat 336® (Q^+Cl^-), bonds to the catecholborane which introduces a negative charge on boron. Also, in solution $RhCl_3$ combines with Q^+Cl^- and forms a $Q^+RhCl_4^-$ complex. Then a chloride ion dissociates from the $RhCl_4$, and this is followed by association of a 1-octene molecule to form the complex 1. After that the negatively charged boron species adds to the secondary carbon to form species 2 which goes on to form the intermediate 3. Intermediate 3 is oxidized by

alkaline H_2O_2 to 2-octanol and regenerates the $RhCl_3$ catalyst. The source of the proton at C-1 in the final 2-octanol product is apparently the alkaline hydrogen peroxide. The results of hydroboration of 1-octene with catecholborane in the presence of $RhCl_3$ -Aliquat 336® catalyst (using methylene chloride as solvent) are summarized in Table 1.

Table 1. Hydroboration of 1-Octene with Catecholborane in the Presence of $RhCl_3$-Aliquat 336® Catalyst, Using Methylene Chloride as the Solvent

Exp #	moles of $RhCl_3$	moles of Q^+Cl^-	moles of CB	moles of 1-octene	T(C°)	hours	product ratio (±1%) GC* NMR	yield%
1.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.01	0.01	33	10	P_1=25 P_1=40 P_2=75 P_2=60	
2.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.05	0.01	33	10	P_1=5 P_1=12 P_2=95 P_2=88	18.0±1%[a]
3.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.01	0.01	33	10	P_1=5 P_2=95	10.3±1%[a]
4.	none	$1.1x10^{-3}$	0.03	0.01	21	24	NP	
5.	$2.4x10^{-4}$	none	0.03	0.01	21	5	P_1=87 P_2=13	1.6±1%[b]
6.	$2.4x10^{-4}$	none	0.03	0.01	21	24	P_1=87 P_2=13	35.0±1%[b]
7.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.03	0.01	21	24	P_1=40 P_2=60	45.5±1%[b]
8.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.03	0.01	21	10	P_1=33 P_2=67	65.4±1%[b*]
9.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.03	0.01	21	5	P_1=5 P_2=95	59.3±1%[b*]
10.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.03	0.01	21	5	P_1=5 P_2=95	23.0±1%[b]
11.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.03	0.01	21	5	P_1=5 P_2=95	14.4±1%[b]
12.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.03	0.01	21	2	P_1=5 P_2=95	16.2±1%[b]
13.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.03	1-octanol 0.01 mole	21	24	P_1=100	
14.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.03	2-octanol 0.01 mole	21	24	P_2=100	
15.	0.001	0.001	0.003	0.001	21	5	P_1=59 P_2=41	

Oven temperature: Isothermal at 150° C, injector/detector: 265°C, flow rate: 20 mL/min.

[a]The yields% were determined by weighing.

[b]The yields% were determined using internal standard: 1, 3, 5,-triisoproylbenzene by GC.

b* The yields% were determined using internal standard: 1, 3, 5,-triisoproylbenzene by GC (without LC in the wok up procedures)

Q^+Cl^-=$[CH_3 (CH_2)_7]_3N^+CH_3Cl^-$

CB= Catecholborane

P_1=1-octanol P_2=2-octanol

NP= no product

Hours= length of hydroboration

In experiments 1 and 2 (Table 1 on page 36), the ratios of products for 1-octanol to 2-octanol were 25% to 75% and 5% to 95% respectively. An additional experiment (3,Table 1) suggests that the 5% to 95% ratio is reproducible. The 25% to 75% product ratio of 1-octanol to 2-octanol in experiment 1 is probably not a reliable ratio because this was the first time the reaction was run. The yield for experiment 1 was not measured. The yields for Experiment 2 and 3 were determined by weighing the crude concentrated products after rotary evaporation (withou LC procedures in the work up procedures).

A variety of experiments have been run to determine characteristics of this reaction.

4.1 Study of the Stoichiometry of the Reaction

The stoichiometry of the reaction was studied by varying the number of moles of catecholborane. In experiments 2 and 3 (Table 1), 0.01moles of 1-octene and 0.05 and 0.01 moles of catecholborane were used, respectively. The product ratio remained constant, but the yield when 0.05 moles of catecholborane (Experiment 2, Table 1) was used was larger than when 0.01 moles of catecholborane was used. In the process of adding catecholborane in experiment 2 (0.05 moles), there was no bubbling or heat evolution observed after adding approximately 0.02 moles of catecholborane, suggesting that the alkene had all been consumed. Therefore, 0.03 moles of catecholborane was considered to be adequate, and this amount was used for remaining reactions.

4.2 Determination of Product Ratio

The ratio of 2-octanol to 1-octanol for experiment 2 and 3 (Table 1) determined by GC is 95/5, whereas NMR analysis (integrated area) indicated the ratio to be 88/12. A 95/5 mixture of 2-octanol and 1-octanol was prepared, and NMR analysis yielded a ratio of 2-octanol to 1-octanol of 82/18. GC yielded an ratio of 94/6. This clearly suggests that GC analysis of these alcohols is more accurate than NMR analysis.

4.3 Reaction Studies

The results in Table 1 reveal the significance of $RhCl_3$ in producing octanols. It is clear from Experiment 4 (Table 1) that $RhCl_3$ is necessary to produce alcohols at a meaningful ratio since after 24 hours in the absence of $RhCl_3$ no octanols were formed. Aliquat 336® is necessary for obtaining high yields and a high ratio of 2-octanol to 1-octanol (Experiments 5 and 6 Table 1). The purpose of running experiments 5 and 6 was to test the mechanism of the hydroboration of 1-octene with catecholborane in the presence of $RhCl_3$-Aliquat336® catalyst. This was done by using $RhCl_3$ but no Aliquat 336® catalyst. The ratio of 1-octanol to 2-octanol from experiment 5 and 6 (Table 1) is 87 to 13 without Aliquat 336® phase transfer catalyst. Thus, Aliquat 336® is important for obtaining 2-octanol as the major product.

The reaction may have a temperature dependence (Experiments 2 and 8 Table 1), since the only difference between experiment 2 and experiment 8 was the fact

that the former was run at 33°C (room temperature) and the later at 21°C (room temperature). The ratios of 1-octanol to 2-octanol for experiments 2 and 8 were 5 to 95 and 33 to 67, respectively. Also certain results indicate a time dependence (Experiments 7, 8, and 9). The times of the hydroboration reactions for experiments 7, 8, and 9, were 24, 10, and 5 hours, and the ratios of 1-octanol to 2-octanol were 40 to 60, 33 to 67 and 5 to 95 respectively. In order to test reasons for product ratio changes, experiments 13 and 14 were run (using 1-octanol and 2-octanol as the starting material). This was done to check the stability of 1-octanol and 2-octanol to reaction conditions. The products were analyzed using GC and these showed that 100% of 1-octanol and 2-octanol remained intact. These results suggest that 1- octanol and 2-octanol are stable to the reaction conditions. Therefore, the product ratio changes with changes in reaction times is due to other factors.

In order to check the reproducibility of these reactions, one reaction was run three times under the same conditions (Experiments 9, 10 and 11 Table 1) The ratio of 2-octanol to 1-octanol for the three reactions are all the same 95/5, but the yields for the three experiments are all different. The yield for experiment 9 was 59.3% which is much high than experiments 10 and 11 (the yields for experiments 10 and 11 were 23% and 14% respectively). The work up procedures for the three reactions were all same, except that the last step using liquid chromatography to purify the product was skipped for experiment 9. Low yields for experiments 10 and 11 may thus be due to mechanical loss during liquid chromatography. The yields for experi-

ments 10 and 11 are also different. The average yield for the two experiments is 18.5 and the standard deviation is 6.4.

Experiments 7, 8 and 9 (Table 1) showed that shorter reaction times gave higher product ratio of 2-octanol to 1-octanol. Therefore, experiment 12 (Table 1) was run for 2 hours at room temperature. The ratio of 2-octanol to 1-octanol analyzed by GC was 95 to 5 and that is the same ratio as the reaction run for 5 hours (Experiments 9-11 Table 1). Experiment 15 (Table 1) was run using stoichiometric amount of $RhCl_3$-Aliquat 336® equal to 1-octene (run for 5 hours). The ratio of 1-octanol to 2-octanol was 59 to 41.

4.4 Solvent Effect

Many papers[9, 10] published on hydroboration reactions use THF as a solvent. One advantage of THF solvent is that it undergoes reflux at high temperature, and this may lead to higher yields . In order to test some solvent effects, hydroboration of 1-octene was carried out with catecholborane in the presence of $RhCl_3$-Aliquat 336® catalyst using THF as the solvent. The results are summarized in Table 2.

Table 2. Hydroboration of 1-Octene with Catecholborane in the Presence of $RhCl_3$-Aliquat 336® Catalyst Using THF as the Solvent[22].

Exp#	moles of $RhCl_3$	moles of Q^+Cl^-	moles of CB	moles of 1-octene	T(C°)	hours	product ratio ±1%	yield% GC*
1.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.03	0.01	21	10	P_1=50.0 P_2=50.0	53.5±1%
2.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.03	0.01	21	5	P_1=10.0 P_2=90.0	63.6±1%
3.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.03	0.01	60	5	P_1=4.5 P_2=95.5	11.0±1%

Oven temperature: Isothermal at 150 ^{0} C, injector/detector: 265 ^{0} C, flow rate: 20 mL/min.
*Yield was determined using 1, 3, 5-triisopropylbenzene as an internal standard
Q^+Cl^-=$[CH_3(CH_2)_7]_3N^+CH_3Cl^-$
CB=Catecholborane
P_1=1-octanol
P_2=2-octanol
Hours = length of hydroboration reaction

The three experiments in Table 2 indicate that shorter reaction times again gave the higher product ratio (2-octanol to 1-octanol) consistent with the reaction using methylene chloride as the solvent (Table 1). The product ratio however, is lower than when methylene chloride is used. For example at 21°C, a 10 hour reaction gave a product ratio of 2-octanol to 1-octanol of 67 to 33 (Experiment 8 in Table 1)

when methylene chloride was used as the solvent, but under the same conditions THF solvent gave a ratio of 2-octanol to 1-octanol of 50 to 50 (Experiment 1 in Table 2 on page 41) Another example is the reaction run at 21°C for 5 hours using methylene chloride as solvent, where the product ratio of 2-octanol to 1-octanol was found to be 95 to 5 (Experiments 9, 10 and 11 in Table 1), but using the same conditions with THF as a solvent the product ratio of 2-octanol to 1-octanol was 90 to 10 (Experiment 2 in Table 2 on page 41). Higher temperature apparently favors a higher product ratio of 2-octanol to 1-octanol (Experiment 3 in Table 2).

4.5 Using Styrene as the Substrate in $RhCl_3$ -Aliquat 336® Catalyzed Hydroborations

In 1990, Lixin Dai[9] and his co-workers have found that hydroboration of styrene with catecholborane in the presence of Wilkinson's catalyst gives Markovnikov addition as the major product. Therefore, hydroboration with catecholborane using styrene as the starting material in the presence of $RhCl_3$-Aliquat 336® catalyst was tried. The product ratio of α-phenylethyl alcohol to β-phenylethyl alcohol was analyzed by GC and is displayed on Table 3.

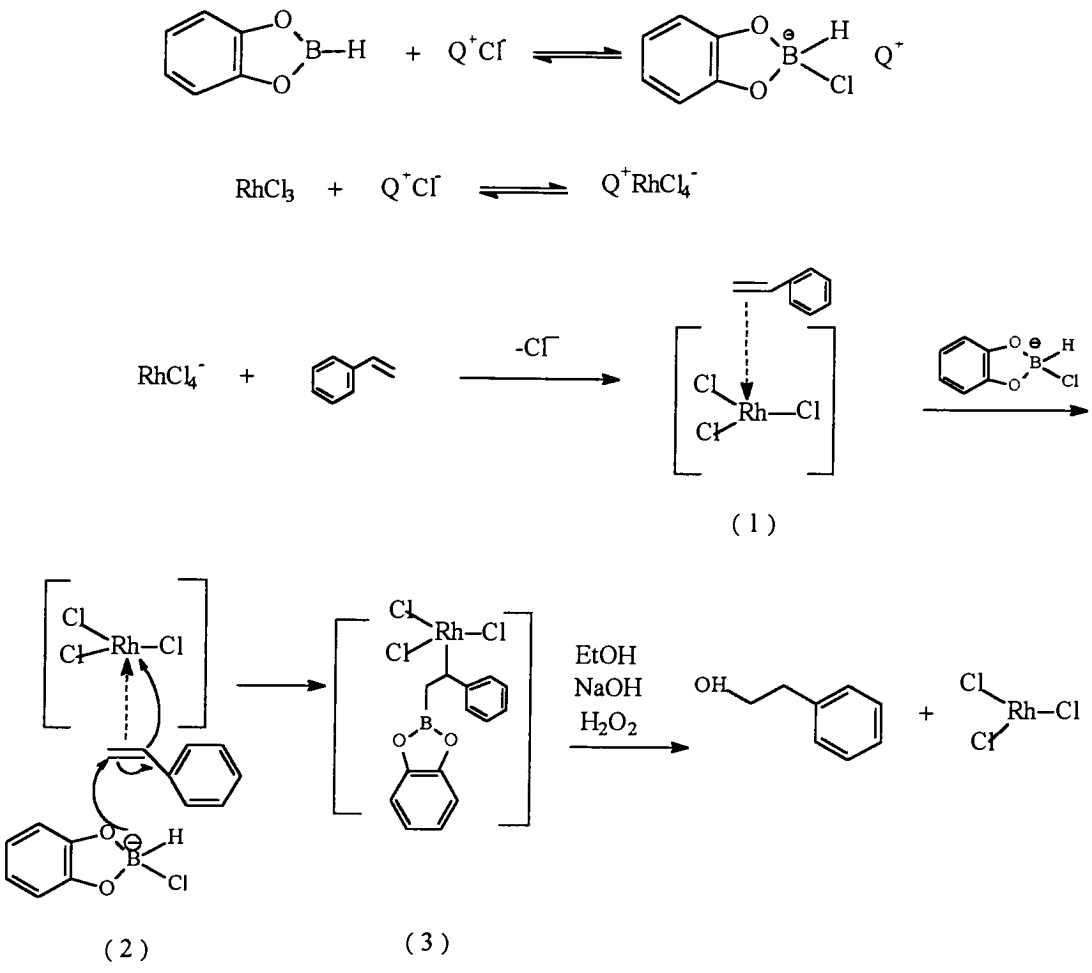
Table 3. Hydroboration of Styrene with Catecholborane in the Presence of $RhCl_3$-Aliquat 336 ® Catalyst, Using Methylene Chloride as the Solvent

Exp#	moles of $RhCl_3$	moles of Q^+Cl^-	moles of CB	moles of styrene	T(C°)	hours	product ratio ±1%	yield% GC*
1.	$2.4x10^{-4}$	$1.1x10^{-3}$	0.03	0.01	21	5	P_1=80.0 P_2=20.0	12.0±1%
2.[23]	$2.4x10^{-4}$	$1.1x10^{-3}$	0.03	0.01	21	5	P_1=86.0 P_2=14.0	33.0±1%

Oven temperature: Isothermal at 150 ^{0} C, injector/detector: 265 ^{0} C, flow rate: 20 mL/min.
*Yield was determined using 1, 3, 5-triisopropylbenzene as an internal standard
Q^+Cl^-=$[CH_3(CH_2)_7]_3N^+CH_3Cl^-$
CB=Catecholborane
P_1=β-phenylethyl
P_2=α-phenylethyl
Hours=length of hydroboration reaction

Table 3 shows a high proportion of *anti*-Markovnikov addition, which is opposite to the hydroboration of styrene with catecholborane in the presence Wilkinson's catalyst discovered by Lixin Dai.[4]

The proposed mechanism is as follows:



In solution, a chloride ion from Aliquat 336® (Q^+Cl^-), bonds to the catecholborane which introduces a negative charge on boron. Also, in solution $RhCl_3$ combines with $Q^+ Cl^-$ to form the $Q^+RhCl_4^-$ complex. Then a chloride ion dissociated from $RhCl_4^-$ and this is followed by association of a molecule of styrene to form the complex 1. After that the negatively charged boron bonds to the associated styrene and because

of the large steric effect of the phenyl group the boron bonds to the terminal (β) carbon of styrene (structure 2) and eventually this produces intermediate 3. After the oxidation, a primary alcohol, 1-octanol, is formed due to the earlier *anti*-Markovnikov hydroboration.

Commercial styrene was used as the starting material in these reactions. There is 5-10 ppm inhibitor (tert-butylcatechol) present in the styrene to prevent styrene from polymerizing. To test whether the inhibitor affects the hydroboration, reactions were run using styrene both in the presence and absence of inhibitor, the reaction using styrene in the presence of inhibitor was run twice. The product ratio of α- phenylethyl alcohol to β-phenylethyl alcohol for experiments 1 and 2 in Table 3 were 20 to 80 and 14 to 86 and the yields 12% and 33% respectively. The reaction without inhibitor has not yet been run. The inhibitor may be taken out of the styrene solution before running a reaction. There are two ways to remove the inhibitor from the styrene solution. One is by using fractional distillation, since the boiling point of styrene is 145°C while the boiling point of the inhibitor is 285°C, and the other way is by using a disposable column to filter out the inhibitor. Such a filter is available from Aldrich Chemical company (inhibitor remover).

Reviewing the results in Table 1 suggests that hydroboration with catecholborane in the presence of $RhCl_3$-Aliquat 336® using methylene chloride as the solvent is a very useful reaction. We obtain a high ratio of 2-octanol to 1-octanol (95/5) and a high yield 59% when the reaction is done for 5 hours at 21°C (Experiment 9, Table 1). These reactions are very useful, because they give a large predominance of Mark-

ovnikov product. The results in Table 2 suggest use of THF as the solvent for the rhodium-catalyzed hydroboration reaction also gives a good yield (Experiment 1 and 2 in Table 2), and the product ratio again favors 2-octanol.

In general, these reactions are very sensitive to reaction time and temperature. Yields are sometimes low and sometimes difficult to reproduce, this is likely due to variation in mechanical losses.

Though hydroboration reactions have been studied extensively, rhodium catalyzed hydroboration reactions are relatively new. Blum discovered that the catalyst $RhCl_3$-Aliquat 336® reduced aromatics to cyclohexane derivatives using phase transfer catalysts under very mild conditions.[13] We find that hydroboration of 1-octene with catecholborane in the presence of the same catalyst ($RhCl_3$-Aliquat 336®) in anhydrous organic solvents also yields novel results. We found out that the Aliquat 336® ion pair is very important for obtaining 2-octanol as major product in the reaction of 1-octene with catecholborane in the presence of $RhCl_3$ catalyst. Lixin Dai[9] found that in the hydroboration of styrene and substituted styrene, with catecholborane in the presence of Wilkinson's catalyst, the α-alcohol is obtained as the major product. The mechanism[11] proposed for explaining the Markovnikov addition is that the double bond in styrene is next to the benzene ring so that a η^3 intermediate formed which formed a secondary organoborane and after an oxidation step α-alcohol is formed. The reaction[21] of 1-octene with catecholborane in the presence of Wilkinson's catalyst gives as the major product 1-octanol, which is the result of an *anti*-Markovnikov addition. When the catalyst is changed to $RhCl_3$-Aliquat 336® the major product is 2-

octanol which is a Markonikov addition. Experiments 5 and 6 (Table 1 on page 36) show that in order to get 2-octanol as the major product, the Aliquat 336® ion pair is necessary for the reaction. The mechanism we proposed for the results (page 34) indicates that a chloride ion in the Aliquat 336® ion pair bonds to the catecholborane which introduces a negative charge on the boron, the negatively charged boron species then bonds to the secondary carbon of 1-octene so the major product should be a secondary alcohol after oxidation step Therefore, the ion pair formed from rhodium trichloride and Aliquat 336® is a very unusual catalyst

This mechanism is proposed based only on the results obtained from this research. Continued study of the novel catalyst $RhCl_3$-Aliquat 336®, may clarify the detailed mechanism of the novel results from this research and other results using this catalyst.

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